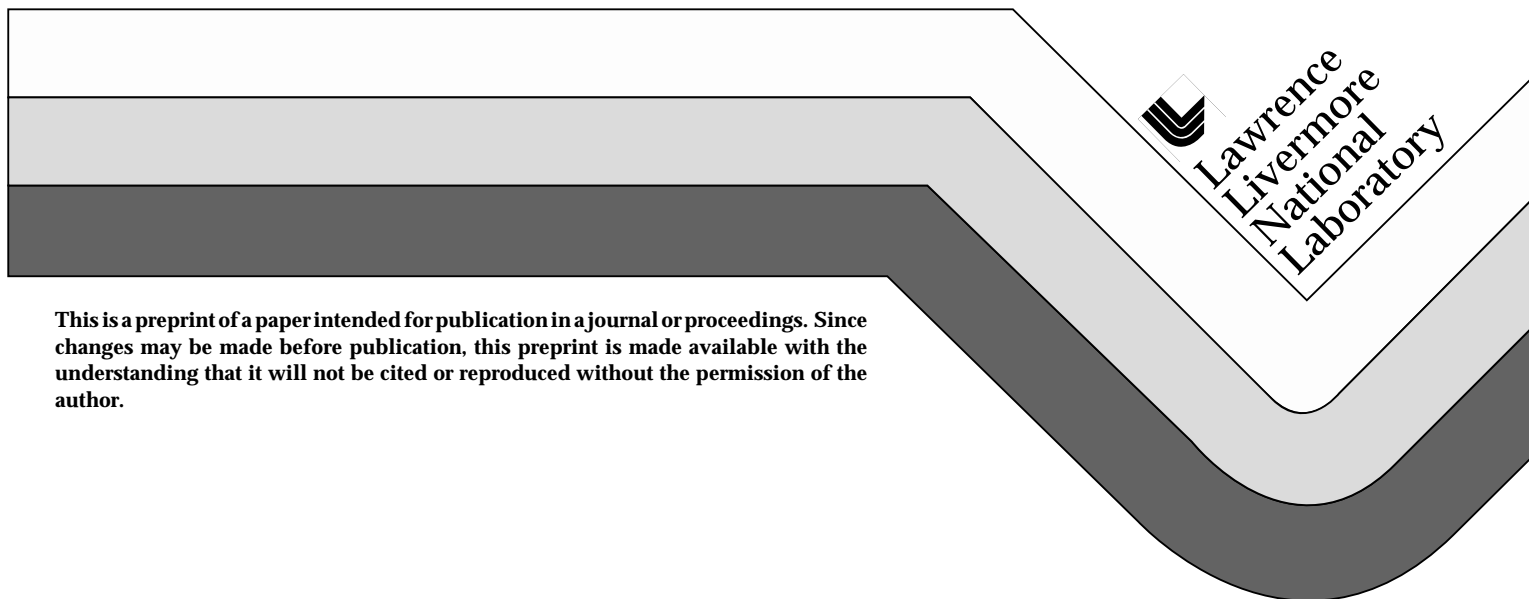


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LITHIUM INTERCALATION IN POROUS CARBON ANODES

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ABSTRACT

Carbon foams derived from the phase separation of polyacrylonitrile/solvent mixtures were investigated as lithium intercalation anodes for rechargeable lithium-ion batteries. The carbon foams have a bulk density of 0.35-0.5 g/cm³, low surface area (< 50 m²/g), and an average cell size of 5-10 μm. Polyacrylonitrile-based carbon foams doped with phosphoric acid had capacity as high as 450 mAh/g. Carbon capacity increased with increasing phosphoric acid concentration in the doping solution. The doped porous carbon anodes exhibited good cyclability and excellent coulombic efficiency.

INTRODUCTION

A variety of carbonaceous materials (petroleum cokes, carbon blacks, carbon fibers, graphites, etc.) have been used as lithium intercalation anodes in lithium-ion or rocking-chair rechargeable cells [1, 2]. Many of these types of materials have capacity below the theoretical value of 372 mAh/g which corresponds to 1 mole of lithium per 6 moles of carbon (LiC_6). One of the means for increasing the carbon capacity is to dope it with phosphorus [3, 4, 5]. Omaru and co-workers [3, 4], for example, have shown that the presence of phosphorus in their polyfurfuryl alcohol-based carbons enhanced the electrode capacity by as much as 30% to 450 mAh/g. Work in our laboratories with various types of phosphorus-doped carbons also showed increased capacities [5, 6]. Here we report recent results on the influence of a phosphorus additive on the ability of monolithic polyacrylonitrile-derived porous carbon foams to intercalate lithium. These types of carbon foams with controlled morphology and added phosphorus dopant are expected to provide enhanced electrode performance. This work is part of a broader effort directed at developing an understanding of how foam morphology, chemical composition and local structural order affect electrochemical performance.

EXPERIMENTAL

Porous carbon electrodes were prepared as follows. Polyacrylonitrile (PAN Type A; Dupont) was dissolved in a 97:3 mixture of dimethylsulfoxide/water at elevated temperature in a closed vessel. This slightly yellow solution was then poured over a piece of carbon paper (grade 50; Lydall Corp) lying on a copper plate. A pre-heated glass plate was used to cover the carbon paper and uniformly spread the PAN solution. The copper plate was then placed in contact with an ethanol slush bath at $-80\text{ }^{\circ}\text{C}$ to induce phase separation and freeze the solvent mixture. The frozen PAN/carbon paper composite was then placed in methanol and allowed to warm to room temperature. After several solvent exchanges with fresh methanol, the specimens were dried in a circulating oven at $50\text{--}85^{\circ}\text{C}$. In certain cases, a phosphoric acid/methanol solution was used prior to drying to achieve doped specimens. All specimens were then pyrolyzed in an inert atmosphere for 4 hours at $1050\text{ }^{\circ}\text{C}$ using a ramp cycle of $\sim 1^{\circ}\text{C}/\text{min}$. The presence of the Lydall carbon paper prevented the large amounts of macroscopic shrinkage normally associated with the pyrolysis of PAN foams.

Electrochemical studies were performed using a 64-channel Maccor battery tester. The experiments were carried out in a 15 ml, three-electrode cylindrical cell in which the electrodes and separator were positioned horizontally and stacked vertically. The geometric surface area of the working electrode was 1.12 cm^2 . A composite of lithiated carbon paper and lithium foil (Cyprus Foote Mineral) was used as the counter electrode and lithium foil was used as the reference electrode. Whatman fiberglass filters (934-AH) were used as separators between the working and counter electrodes. The electrolyte was 0.45 M lithium

trifluoromethanesulfonimide, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, (tradename HQ115, 3M Corp) and 0.05 M LiAsF_6 (FMC Corp) in propylene carbonate (Grant Chemical). The cells were constructed and tested at $16 \pm 2^\circ\text{C}$ in a dry argon-atmosphere glove box (< 10 ppm water). The cell was charged at constant-current rate corresponding to 1 mole of lithium per 6 moles of carbon in 24 hours (C/24) to a cut-off voltage of 0.005V (Li^+/Li) and held at this potential for 4 hours. It was then discharged at the same rate to 1.5 V and held there for another 4 hours. This procedure was used to assure complete lithium intercalation/deintercalation. After 4 cycles, the rate was increased to C/8 (i.e., 1 mole of Li per 6 moles of carbon in 8 hours) for further cycle life study.

The x-ray diffraction (XRD) analyses were performed using a diffractometer (Siemens Diffractometer OSP, Model:D500, Germany). The samples were first ground to a fine powder, and then placed on a double-sided tape that was stuck to a glass slide which served as the specimen holder. Step-scanned intensity data were generated using $\text{CuK}\alpha$ radiation at a voltage of 40 kV and current of 30 mA. The data were gathered at room temperature over a 2θ range from 20° to 60° and 2-s count time at each step. SEM observations were performed using a Hitachi S570 Scanning Electron Microscope.

RESULTS AND DISCUSSION

The porous carbon electrodes used here have bulk density of between 0.35 to 0.5 g/cc. BET surface areas are relatively low ($< 50 \text{ m}^2/\text{g}$) and minimize the first cycle irreversible capacity loss associated with the formation of a passivating film at the carbon/electrolyte interface. SEM observations show that the monolithic carbon/fiber structure consists of interconnected cells (i.e., voids) with average diameter between 5-10 μm .

Representative potential-capacity profiles for the intercalation and de-intercalation of Li in carbonized PAN anodes with and without phosphorus are presented in Figure 1. The curves indicate that the potential for de-intercalation, at a given capacity, is lower for the phosphorus-doped carbon. The increased capacity in this fashion is expected to give lithium-ion cells with a higher average cell voltage. There is evidence of a slight plateau in the curve for the phosphorus-doped materials during deintercalation near 0.8 V as can be seen in Figure 1. A similar plateau was also observed by us [5, 6] and Omaru *et al.* [3, 4] with various types of phosphorus-doped carbons.

The variation in the lithium-intercalation capacity with the relative phosphorus doping concentrations is shown in Figure 2. The reversible capacity of doped carbon anodes increases with increasing phosphoric acid concentration in the doping solution and appears to reach a plateau value near 450 mAh/g. For example, the capacity of an electrode immersed in 0.066g $\text{H}_3\text{PO}_4/\text{ml}$ methanol solution prior to pyrolysis increases by more than 50% to 445 mAh/g (x in $\text{Li}_x\text{C}_6 = 1.19$). Electrodes treated with solution of higher phosphoric acid concentration also

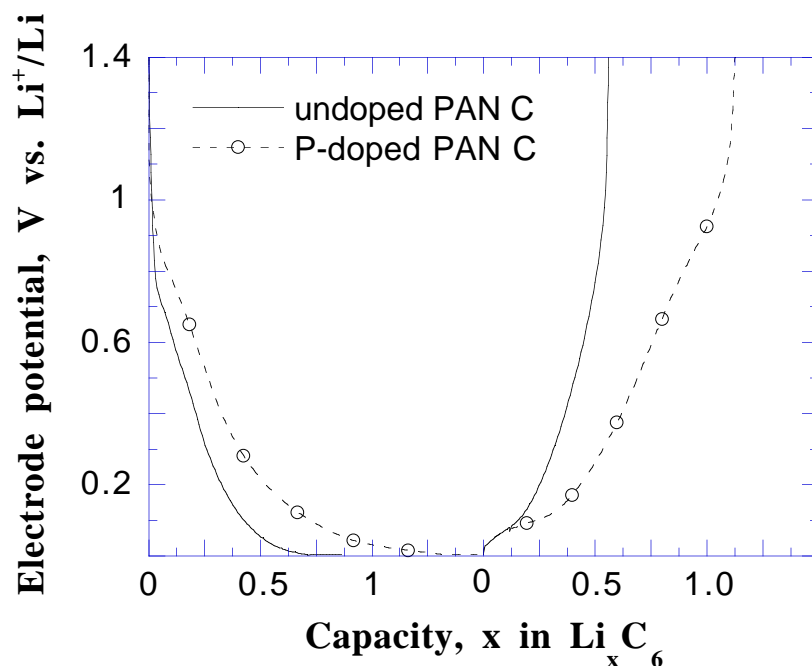


Figure1. Comparison of discharge/charge profiles of undoped versus P-doped porous carbon. Doped electrode immersed in 0.022 g H_3PO_4 / ml methanol solution prior to pyrolysis. Electrolyte, 0.45M $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and 0.05M LiAsF_6 in PC. C/24 rate. T, 16°C.

showed large capacity increase. The performance of these doped carbons exceeds that of commercial carbons and graphites that we have investigated earlier [6]. Quantitative data on the phosphorus content in these samples are not yet available, although energy dispersive X-Ray analysis clearly reveals the presence of phosphorus. The first cycle irreversible capacity loss associated with passivated film formation appears to decrease somewhat with doped samples. Similar trends in the electrode behavior have been observed with P doped-petroleum cokes although the increase in the capacities of the doped coke samples were not as large [5].

The impregnation of the porous PAN/fiber precursor with phosphoric acid prior to pyrolysis may lead to deposition of phosphorus-containing species on the inner carbon surface. However, this has not yet been experimentally verified. The XRD results indicated that the d(002) spacing of the undoped PAN carbons was 0.360 nm. The phosphorus-doped samples showed no measurable change in d(002) spacing. Using high-resolution NMR and XPS, Omaru and co-workers (3, 4) suggested that phosphorus exists in their samples as a compound of the form $(\text{C}_6\text{H}_5\text{O})_2\text{P}(=\text{O})\text{OH}$. Other studies (8-10) suggest that P-O species are likely to be present after impregnation of carbon with phosphorus compounds and subsequent heat treatment. These species are believed to be bonded to the surface of the carbonaceous material at the edge-plane sites. Oh and Rodriguez (10) suggested that phosphorus is incorporated into the structure at the edge-plane sites of their carbon particles. Since phosphorus has a larger atomic size (0.106 versus

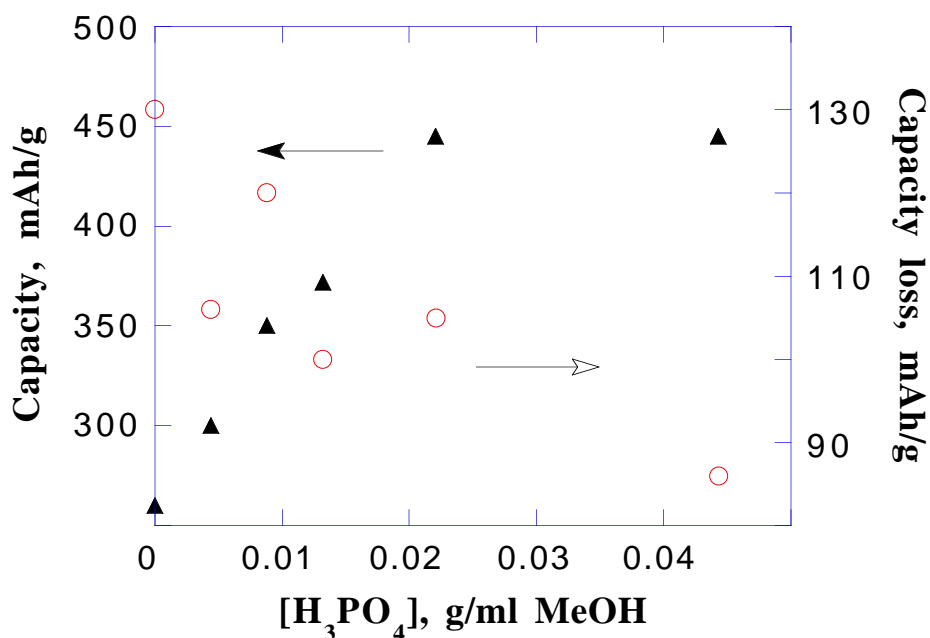


Figure 2. Capacity and irreversible capacity loss as a function of phosphoric acid concentration in the doping solution. First cycle data. Electrolyte, 0.45M LiN(CF₃SO₂)₂ and 0.05M LiAsF₆ in PC. Rate, C/24. Temp, 16°C.

0.077 nm) than carbon (10), it is conceivable that the phosphorus atoms at the edge-plane sites may serve to expand the layer planes at the surface of the particles and facilitate intercalation by lithium. The XRD results appear to be consistent with this type of surface effect; however, further work is needed to delineate the role of phosphorus in lithium intercalation.

The undoped and doped PAN-derived carbon anodes described in this work show excellent cycle-life performance with coulombic efficiency close to 100%. PAN-derived porous carbons have been cycled for over 100 cycles in our laboratory with less than 10% drop in reversible capacity. Phosphorus doped materials were also found to have stable performance. The performance of a doped anode as a function of cycle life is shown in Figure 3. As can be seen from the figure, the reversible capacity decreases by less than 10% after 72 cycles with coulombic efficiency greater than 99%.

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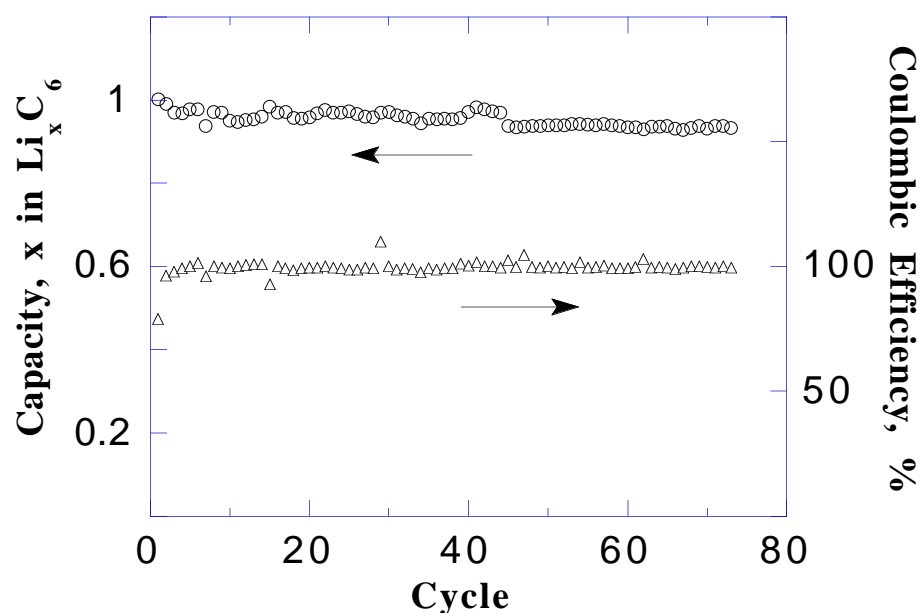


Figure 3. Electrochemical performance of PAN-derived carbon anodes treated in a 0.013g H_3PO_4 /ml methanol solution before pyrolysis. Electrolyte, 0.45M $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and 0.05M LiAsF_6 in PC. Rate, C/24. T, 16°C.

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